

IAP2 Rec'd PCT/PTO 27 SEP 2006

## DESCRIPTION

A HIGH-STRENGTH THICK STEEL PLATE EXCELLENT IN LOW  
TEMPERATURE TOUGHNESS AT HEAT AFFECTED ZONE RESULTING  
5 FROM LARGE HEAT INPUT WELDING

## BACKGROUND OF THE INVENTION

## 1. Field of the invention

10 The present invention relates to a high  
strength thick steel plate excellent in low temperature  
toughness at heat affected zone (hereinafter referred to  
as an "HAZ") used for ships, offshore structures,  
medium/high rise buildings, bridges, and so forth, more  
15 particularly relates to a steel plate having a thickness  
of 50 mm or more and a tensile strength of 490 to 570 MPa  
and having an excellent welded joint even in a case where  
welding with a welding heat input of 20 to 100 kJ/mm is  
conducted.

## 20 2. Description of the Related

In recent years, the demands on the material  
properties of steel materials for welding used in large  
sized structures such as ships, offshore structures,  
medium/high rise buildings, and bridges have become  
25 increasingly tough. Especially, among these structures,  
the use of steel plates having large thicknesses  
exceeding 50 mm and having tensile strength of around 570  
MPa has been increasing. Further, in order to promote  
higher efficiency of the welding, for the welding of such  
30 high-strength thick steel plates, one-pass welding by a  
large heat input welding process such as electro-gas  
welding, electro-slag welding, etc. has been investigated.  
The demands on the HAZ toughness have become increasingly  
tough in the same way as on the toughness of the base  
35 material per se.

Many proposals have been made hitherto paying  
attention to the HAZ toughness of steel plate to which a

large heat input welding process is applied. For example, Japanese Unexamined Patent Publication (Kokai) No. 55-026164 discloses an invention of securing fine Ti nitrides in the steel so as to reduce the austenite grain size in the HAZ and thereby improve the toughness.

Further, Japanese Unexamined Patent Publication (Kokai) No. 03-264614 proposes an invention making use of complex precipitates of Ti nitrides and MnS as transformation nuclei of ferrite so as to improve the HAZ toughness.

Further, Japanese Unexamined Patent Publication (Kokai) No. 04-143246 proposes an invention making use of complex precipitates of Ti nitrides and BN as precipitation nuclei of grain boundary ferrite so as to improve the HAZ toughness.

However, Ti nitrides end up becoming almost completely dissolved in the vicinity of the border with a welded metal in HAZ where the highest temperature reached exceeds 1400°C (hereinafter also referred to as a "weld bond portion"). As a result, there is a problem that the effect of improvement of the toughness is lowered. For this reason, in steel utilizing the Ti nitrides as described above, it is difficult to meet the recent tough demands for the HAZ toughness or the required characteristics of the HAZ toughness in ultra-large heat input welding.

Steels containing Ti oxides as a method of improving the toughness in the vicinity of this weld bond portion are being used in various fields such as thick plates and steel shapes. For example, in the field of thick steel plates, as described in the inventions disclosed in Japanese Unexamined Patent Publication (Kokai) No. 61-079745 and Japanese Unexamined Patent Publication (Kokai) No. 61-117245, steel containing Ti oxides is very effective for improving toughness at the large heat input weld portion, and is promising in application to high tensile steels. This principle is that the Ti nitrides, MnS, etc. precipitate in the middle

of temperature drop after welding using the Ti oxides stable even at the melting point of the steel as precipitation sites, fine ferrite is generated using these as sites, and as a result the production of coarse ferrite harmful to the toughness is suppressed and deterioration of the toughness can be prevented.

However, such Ti oxides involve a problem that the number of particles dispersed into the steel cannot be increased that much. The reason is the coarsening or aggregation of the Ti oxides. It is believed that if the Ti oxides particles are increased, coarse Ti oxide particles of 5  $\mu\text{m}$  or more, i.e., so-called inclusions, end up increasing. These inclusions of 5  $\mu\text{m}$  or more size become initiation sites for fracture of a structure or cause a drop of the toughness and therefore are harmful. Therefore, this should be avoided. For this reason, in order to achieve a further improvement of the HAZ toughness, it was necessary to make use of oxides which are hard to coarsen and agglomerate and are more finely dispersed than Ti oxides.

Further, many such methods of dispersion of such Ti oxides into steel are based on adding Ti into molten steel substantially not containing any Al or other strong deoxidizing elements. However, it is difficult to control the number and degree of dispersion of Ti oxide particles in steel by just adding Ti into the melt. Further, it is also difficult to control the number and degree of dispersion of precipitates such as TiN and MnS. For this reason, in steel in which Ti oxide particles are dispersed by only Ti deoxidation, there was the problem for example that neither a sufficient number of Ti oxide particles nor a stable toughness of thick plate in the thickness direction could be obtained.

With respect to such problems, Japanese Unexamined Patent Publication (Kokai) No. 06-293937 and Japanese Unexamined Patent Publication (Kokai) No. 10-183295 disclose inventions making use of Ti-Al complex

oxides and Ti, Al, and Ca complex oxides produced by the addition of Al immediately after the addition of Ti or the complex addition of Al and Ca. By such inventions, it became possible to greatly improve HAZ toughness in the large heat input welding.

#### SUMMARY OF THE INVENTION

However, with the conventional means of reducing the austenite grain size of the HAZ or generating ferrite by using precipitates as transformation nuclei of the ferrite, it is necessary to increase the alloy elements in order to secure a tensile strength of 490 MPa or more when the plate thickness is 50 mm or more. In this case, the hardness of the HAZ rises and, at the same time, the production of MA (martensite-austenite constituent) degrading the toughness becomes remarkable. Therefore, a sufficient HAZ toughness such as the E grade (-20°C guarantee) in for example the shipbuilding field cannot be stably secured. In addition, when the tensile strength becomes more than 570 MPa, the required HAZ toughness cannot be obtained.

Therefore, an object of the present invention is to provide a high-strength thick steel plate excellent in the low temperature toughness of the heat affected zone resulting from large heat input welding, which can realize excellent HAZ toughness even in a case of welding with a heat input of 20 to 100 kJ/mm for steel plate having a thickness of 50 to 80 mm, and a tensile strength of 490 to 570 MPa.

The inventors discovered that by defining the amount of addition of Ni and Ni/Mn ratio, the above problems could be advantageously solved. They engaged in extensive study and thereby completed the present invention for the first time. The gist thereof is as follows:

(1) A high-strength thick steel plate excellent in low temperature toughness at a heat affected zone resulting from large heat input welding characterized by containing, by wt%, 0.03-0.14% of C, 0.30% or less of Si,

0.8-2.0% of Mn, 0.02% or less of P, 0.005% or less of S, 0.001-0.040% of Al, 0.0010-0.0100% of N, 0.8-4.0% of Ni, 0.005-0.030% of Ti, and 0.003-0.040% of Nb, where Ni and Mn satisfy Equation [1], and a balance of iron and unavoidable impurities:

$$\text{Ni/Mn} \geq 10 \times \text{Ceq} - 3 \quad (0.36 < \text{Ceq} < 0.42) \quad [1]$$

$$\text{where, } \text{Ceq} = \text{C} + \text{Mn}/6 + (\text{Cr} + \text{Mo} + \text{V})/5 + (\text{Ni} + \text{Cu})/15$$

(2) A high-strength thick steel plate excellent in low temperature toughness at a heat affected zone resulting from large heat input welding as set forth in (1), characterized by further containing, by wt%, one or more of 0.0003-0.0050% of Ca, 0.0003-0.0050% of Mg, 0.001-0.030% of an REM and containing at least 100/mm<sup>2</sup> of grains of an oxide containing 0.0010-0.0050% of O and having an equivalent circle diameter of 0.005 to 0.5  $\mu\text{m}$ .

(3) A high-strength thick steel plate excellent in low temperature toughness at a heat affected zone resulting from large heat input welding as set forth in (1) or (2), characterized by further containing, by wt%, 0.0005-0.0050% of B.

(4) A high-strength thick steel plate excellent in low temperature toughness at a heat affected zone resulting from large heat input welding as set forth in any one of (1) to (3), characterized by further containing, by wt%, one or more of 0.1-0.5% of Cr, 0.01-0.5% of Mo, 0.005-0.10% of V, and 0.1-1.0% of Cu.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of a welding heat cycle corresponding to 45 kJ/mm.

FIG. 2 is a graph of the relationships among Ni/Mn, Ceq, and the simulated HAZ toughness.

FIG. 3 is a graph of an effect of improvement of the simulated HAZ toughness due to dispersion of fine oxides or B addition.

#### BEST MODE FOR CARRYING OUT THE INVENTION

A detailed explanation of the present invention will be given below.

Hitherto, as the means for improving the HAZ toughness, as previously mentioned, it has been considered to suppress an austenite grain growth at a high temperature. The most effective method as that means is pinning an austenite grain boundaries by dispersed particles so as to stop the movement of the grain boundaries. This pinning is extremely effective for reduction of the reheated austenite grain size at the HAZ even in the case where a large heat input such as 20 to 100 kJ/mm is applied. However, in steel material wherein the amount of alloy elements added is increased in order to raise the strength and a carbon equivalent (Ceq) indicating both the weldability of the steel and a quench bardenability in terms of chemical composition becomes 0.36 or more, the hardness of the HAZ becomes higher. Therefore, there arises the new problem that a sufficient HAZ toughness cannot be obtained even when the re-heated austenite grains become finer due to the pinning. In the case where the hardness of the HAZ becomes high, it is necessary to improve the toughness of the base material per se.

Therefore, the inventors intensively studied the optimal chemical composition for improving the toughness of the base material itself for improvement of the HAZ toughness in the case where the Ceq was as high as 0.36 to 0.42, which becomes necessary for the high-strength thick steel plate. It has been conventionally known that Ni is an effective element improving the toughness of the matrix. However, it has not been known whether it is effective for improving the HAZ toughness in case of a high Ceq of 0.36 to 0.42. Therefore, the inventors first studied the influence of the amount of the Ni addition. For the study, they predetermined that an 0.003% or more of Nb addition is effective for securing the base material strength. For evaluation of the HAZ toughness, they employed the ductility/brittleness transition temperature in a Charpy impact test (vTrs) when imparting

a heat cycle corresponding to electro-gas welding (heat input of 45 kJ/mm) shown in FIG. 1.

As a result of their studying the influence of the amount of addition of Ni, first they learned that the required toughness could not be obtained when the Ni was less than 0.8%. Further, even when the Ni was 0.8% or more, they observed cases where the HAZ toughness was not improved and cases where conversely the HAZ toughness was lowered. Therefore, they engaged in further intensive studies including the relationships with the other added elements and Ceq. As a result, they discovered that the HAZ toughness was related to the Ceq and Ni/Mn ratio as shown in FIG. 2 when the Ceq is 0.36 to 0.42 in this way. FIG. 2 plots the synthetic HAZ toughness (vTrs) of the steel material used for the study classified for each Ceq with the Ni/Mn ratio plotted on the abscissa. From FIG. 2, in steel wherein the following relationship stands:

$$\text{Ni/Mn} \geq 10 \times \text{Ceq} - 3 \quad [1]$$

a good toughness in terms of vTrs of -15°C or less was obtained. As the reason why steel not satisfying equation [1] cannot obtain a sufficient HAZ toughness, it can be considered that the amount of addition of Ni is not sufficient and the effect of increasing the toughness of the matrix is small, or that even if a large amount of Ni is contained, MA is produced in the HAZ due to an excessive addition of Mn and the effect of Ni of increasing the toughness disappears. Note that the inventors engaged in a similar study on the heat cycle of the heat input corresponding to a heat input of 100 kJ/mm for the steel used in the above described study, and as a result confirmed that a good synthetic HAZ toughness is obtained in steel satisfying the relationship of equation [1] even in the case of a heat input of 100 kJ/mm.

By the above mentioned studies, the inventors found that the HAZ toughness was improved by the addition of Ni in an amount of 0.8% or more satisfying equation [1]. The inventors further studied regarding the improvement of

the HAZ toughness. They studied the following three methods as methods of improving the HAZ toughness. First is the method of suppressing the coarsening of the austenite grains at a high temperature, since in large heat input welding, the holding time at a high temperature becomes a long period. Therefore, the austenite grains coarsen, which lowers the HAZ toughness. Second is the method of suppressing the coarsening of the grain boundary ferrite, since the cooling time after the welding is long in large heat input welding, so the ferrite generated from the austenite grain boundaries coarsen. The coarse grain boundary ferrite becomes the cause of a drop in the HAZ toughness. Third is the method of refining the HAZ microstructure itself.

Concerning the first method of suppressing the coarsening of the austenite grains, for example, as described in Japanese Unexamined Patent Publication (Kokai) No. 10-183295, the method of dispersing fine oxides is effective. In this publication, in the dispersion of the fine oxides, the amount of dissolved oxygen in the steel melt is adjusted by an equilibrium reaction with Si in the deoxidation process. Further, the following deoxidation is conducted in a sequence of Ti, Al, and Ca. Then, by this method, oxides having a particle size of 0.01-1.0  $\mu\text{m}$  are dispersed to  $5 \times 10^3$  to  $1 \times 10^5/\text{mm}^2$ .

Therefore, the inventors intensively studied a method of further improving the HAZ toughness by dispersing fine oxides in a process containing 0.03% of Nb and adding 0.8% or more of Ni in the case of a Ceq as high as 0.36 to 0.42. First, for the method of dispersing fine oxides, they found the fact that, in such a process, by adjusting the amount of dissolved oxygen of the steel melt to 0.0010-0.0050% in the deoxidation process, then first deoxidizing the steel melt with Ti, and then deoxidizing the steel melt with Al, and further adding one or more of Ca, Mg, and REM, it is possible to



disperse fine oxide particles having an equivalent circle diameter of 0.005 to 0.5  $\mu\text{m}$  to 100/ $\text{mm}^2$  or more. Further, by this dispersion of the fine oxides, the coarsening of the austenite grains at the holding time at a high temperature in the welding was suppressed, and the HAZ toughness could be further improved. As an example, the result of comparison with the HAZ toughness obtained by only adding a proper amount of Ni is shown in FIG. 3. Note that, the larger the amount of Ni, the finer the produced oxides, and the larger the number of particles. When the amount of Ni is 1.5% or more, it even becomes 1000/ $\text{mm}^2$  or more. This is discovered this time. Further, for the amount of Si in the steel melt, the larger the amount of Si, the harder the oxide to form. Therefore, it was clarified from this study that the amount of Si was preferably 0.30% or less and further preferably 0.20% or less. On the other hand, in the case where the amount of dissolved oxygen before the Ti deoxidation exceeds 0.050% and the case where the sequence of the deoxidation elements is different, the oxide coarsens and the sufficient amount of fine oxide cannot be obtained. Therefore, almost no effect of suppression of coarsening of the austenite grains can be obtained. Note that the number of grains of the oxides having the equivalent circle diameter of 0.005 to 0.5  $\mu\text{m}$  was obtained by preparing an extraction replica from the steel plate as the base material. Observing this under an electron microscope with X10000 magnification in at least 100 fields (10000  $\mu\text{m}^2$  or larger observation area), and observing particles less than 0.1  $\mu\text{m}$  by properly raising the magnification. The inventors conducted elemental analysis at each particle having a diameter of 0.005 to 0.5  $\mu\text{m}$  observed and counted the oxide particles.

Next, the inventors intensively studied the suppression of the coarsening of the grain boundary ferrite and the refining of the HAZ microstructure as

above described second and third methods of improvement of the HAZ toughness. As a result, the inventors clarified that the addition of B was effective particularly in the case where large heat input welding corresponding to 20 to 100 kJ/mm was conducted in a process where the  $C_{eq}$  was as high as 0.36 to 0.42 and Ni was added in an amount of 0.8% or more. The reason for that, in terms of the suppression of the coarsening of the grain boundary ferrite, is the suppression of the production of grain boundary ferrite by a segregation of the solute B at the re-heated austenite grain boundaries. Further, in terms of the increased refined HAZ microstructure, in the case where the cooling rate is slow in the large heat input welding, the B nitrides precipitated at the austenite grain boundaries and in the inclusions in the austenite grains due to the addition of B, and a large number of fine ferrite grains of several micrometers using those as nuclei are present at the austenite grain boundaries and in the grains, whereby the HAZ structure is made finer. The inventors compared the improvement of the HAZ toughness by the addition of B with the HAZ toughness obtained by only properly adding Ni. The results are shown in FIG. 3. It is seen that the HAZ toughness is further improved by the addition of B. Further, FIG. 3 shows the HAZ toughness in the case where the B is added in addition to the method of dispersing the above mentioned fine oxides. The HAZ toughness is further improved by the dispersion of the fine oxides and the addition of B. It is considered that the improvement is due to the increase of the oxides acting as precipitation sites of the BN and thereby the greater refined HAZ microstructure due to the increase of the ferrite using the BN as the nuclei.

Further, from the viewpoints of securing the strength and improvement of the corrosion resistance, in addition to the above described conditions, the inventors also studied the HAZ toughness when Cu, Cr, Mo, and V

were added. As a result, they found that the HAZ toughness was not greatly lowered when they were added within ranges of 0.1-0.4%, 0.1-0.5%, 0.03-0.2%, and 0.005-0.050%.

5        Note that, the method of production of the steel plate according to the present invention is not particularly limited. The steel plate may be produced by any known method. For example, a slab is formed from steel melt adjusted to the preferred composition  
10       described above by a continuous casting method, then is heated to 1000 to 1250°C, then is hot rolled.

      Next, an explanation will be given on the reasons for limitation of the ingredients of the steel materials used in the present invention. Below, the wt% in the  
15       compositions will be simply described as %.

      C is an ingredient effective for improving the strength of the steel, so the lower limit is made 0.03%. An excess addition produces large amounts of carbide and MA and remarkably lowers the HAZ toughness, therefore the  
20       upper limit was made 0.14%.

      Si is an ingredient necessary for securing the strength of the base material and deoxidation, but in order to prevent the drop in the toughness due to the hardening of the HAZ, the upper limit was made 0.30%.  
25       When utilizing an oxide, the upper limit of the content is made 0.20% or less in order to prevent the reduction of the oxygen concentration in the molten steel.

      Mn is an ingredient effective for securing the strength and toughness of the base material and must be  
30       added in an amount of 0.8% or more, but the upper limit was made 2.0% within the range where the toughness, cracking property etc. of the welding zone were permissible. Further, concerning the upper limit of Mn, it is necessary to satisfy equation [1] indicating the  
35       relationship among the  $C_{eq}$ , Mn amount, and the Ni amount. This is based on the newly found fact by this study that the increase of Mn becomes the cause of production of a

large amount of MA in the HAZ microstructure in the case where the  $C_{eq}$  is high and the effect of improvement of the HAZ toughness by Ni disappears.

$$Ni/Mn \geq 10 \times C_{eq} - 3 \quad [1]$$

5 P is desirably as little as possible, but in order to reduce this industrially, enormous costs are entailed, so the range of content was made 0.02 or less.

S is desirably as little as possible, but in order to reduce this industrially, enormous costs are entailed, so the range of content was made 0.005 or less.

10 Ni is an important element in the present invention and must be added in an amount of at least 0.8%. Further, concerning the lower limit of Ni, it is necessary to satisfy equation [1] showing the relationship of  $C_{eq}$ , the amount of Mn, and the amount of Ni. The upper limit was made 4.0% from the viewpoint of the production cost.

$$Ni/Mn \geq 10 \times C_{eq} - 3 \quad [1]$$

20 Nb is an element effective for improving the strength of the base material by improving the quench bardenability, so is added in an amount of 0.003% or more. However, if a lot of Nb is added, the MA becomes easy to be produced in the HAZ regardless of the Ni/Mn ratio, while when it is added in an amount larger than 0.040%, a large amount of coarse MA having a long axis of 5  $\mu m$  is produced in the HAZ and greatly reduces the HAZ toughness. Therefore, the upper limit of Nb is made 0.040%. Note that, in order to obtain a higher toughness, preferably the amount of Nb is suppressed to 0.020% or less where almost no coarse MA having a long axis of 5  $\mu m$  is produced in the case of the Ni/Mn ratio satisfying the above mentioned equation [1]. In order to stably obtain further higher toughness, it is preferred to suppress the amount of Nb to 0.010% or less where almost no MA having a long axis of 3  $\mu m$  or more is generated in the case of an Ni/Mn ratio satisfying the above mentioned equation [1].

Al is an important deoxidation element, so the lower limit was made 0.001%. Further, when a large amount of Al is present, the surface quality of the slab is deteriorated, so the upper limit was made 0.040%.

5       Ti is added in an amount of 0.005% or more according to need in order to produce the Ti nitride and the Ti-containing oxide particles which become pinning sites necessary for suppressing the coarsening of the re-heated austenite grains. However, its excess addition increases  
10       the amount of dissolved Ti and induces a drop in the HAZ toughness, therefore 0.030% was made the upper limit.

      N is adjusted in the amount of addition, if necessary, in order to produce the Ti nitride and the B nitride particles at the austenite grain boundaries and  
15       in the grains during the cooling after the welding. In order to form the B nitride by binding with B, N must be added in an amount of 0.0010% or more, but its excess addition increases the amount of dissolved N and induces a drop in the HAZ toughness, so 0.0100% was made the  
20       upper limit.

      Ca is added in an amount of 0.0003% or more, if necessary, in order to produce the Ca-based oxide particles acting as pinning grains necessary for  
25       suppressing the coarsening of the re-heated austenite grains. However, excess addition produces coarse inclusions, so 0.0050% was made the upper limit.

      Mg is added in an amount of 0.0003% or more, if necessary, in order to generate the Mg-based oxide particles acting as pinning grains necessary for  
30       suppressing the coarsening of the re-heated austenite grains. However, excess addition produces coarse inclusions, so 0.0050% was made the upper limit.

      A REM is added in the amount of 0.0001% or more, if necessary, in order to produce the REM-based oxide  
35       particles acting as pinning sites necessary for suppressing the coarsening of the re-heated austenite grains. However, excess addition produces coarse

inclusions, so 0.030% was made the upper limit. Further, the "REM" mentioned here represent Ce and La, and the amount of addition is the total amount of the two.

5 B is added in an amount of 0.0005% or more, if  
necessary, in order to cause the dissolved B to segregate  
at the austenite grain boundaries during the cooling  
after the welding and suppress the production of the  
grain boundary ferrite and further to produce BN at the  
austenite grain boundaries and in the grains. However,  
10 its excess addition increases the amount of dissolved B,  
greatly raises the HAZ hardness, and induces a drop in  
the HAZ toughness, so 0.0050% was made the upper limit.

15 Cu is added in an amount of 0.1% or more, if  
necessary, in order to improve the strength and corrosion  
resistance of the steel. The effect thereof is saturated  
at 1.0%, so the upper limit was made 1.0, but when it  
exceeds 0.4%, MA becomes easy to be generated and the HAZ  
toughness is lowered, therefore 0.4% or less is  
preferred.

20 Cr is added in an amount of 0.1% or more, if  
necessary, in order to improve the corrosion resistance  
of the steel, but its excess addition induces a drop in  
the HAZ toughness due to the generation of MA, so 0.5%  
was made the upper limit.

25 Mo is an element effective for improving the  
strength and the corrosion resistance of the base  
material and is added in an amount of 0.01% or more, if  
necessary. The effect thereof is saturated at 0.5%, so  
the upper limit was made 1.0, but its excess addition  
30 induces a drop in the HAZ toughness due to the generation  
of MA, so 0.2% or less is preferred.

35 V is an element effective for improving the strength  
of the base material and is added in an amount of 0.005%  
or more, if necessary. The effect thereof is saturated at  
0.5%, so the upper limit was made 0.10%, but its excess  
addition induces a drop in the HAZ toughness due to the  
generation of MA, so 0.050% or less is preferred.

### Example 1

Slabs were prepared by continuously casting the steel melt having the chemical compositions shown in Table 1. For D23-D31 and D46-D49, the amounts of dissolved oxygen of the steel melt were adjusted to 0.0010%-0.0050% by Si before charging the Ti, then Ti was used for deoxidization, then Al was used for deoxidation, then any of Ca, Mg, or REM was added for deoxidation. The slabs were re-heated at 1100 to 1250°C, then were hot rolled by the following two methods to produce steel plates having plate thicknesses of 50 to 80 mm. One method was to roll the plate at a surface temperature within a range of 750-900°C, then cool it by water at a plate surface temperature within the temperature range of 200-400°C after recalescence (described as TMCP in Table 2). The other method of production is cooling with water down to room temperature after hot rolling, then tempering within a range of 500-600°C (described as DQ-T in Table 2).

Table 2 shows the production conditions, plate thicknesses, and mechanical properties of the steel plates. Further, for D23-D31 and D46-D49, the numbers of fine oxide particles having equivalent circle diameters of 0.005 to 0.5  $\mu\text{m}$  measured at any location of the steel plates were additionally described. The number of the oxide particles are found by preparing an extraction replica from any portion of the steel plate, observing this under an electron microscope with X10000 magnification in 100 fields or more (10000  $\mu\text{m}^2$  or more in observation area), and observing particles less than 0.1  $\mu\text{m}$  by properly raising the magnification. Elemental analysis was conducted for each observed particle having a diameter of 0.005 to 0.5  $\mu\text{m}$  and the oxide particles were counted. All of the steel plates among D23-D31 and D46-D49 had fine oxide particles having equivalent circle diameters of 0.01 to 0.5  $\mu\text{m}$  dispersed to 100/ $\text{mm}^2$  within

the range of the present invention. Note that it is seen from the comparison of D46 and D47 and D48 and D49 wherein elements other than Si are almost equal, that the smaller the amount of Si, i.e. 0.20% or less, the larger the amount of the oxides.

Each of these steel plates was made to abut against another steel plate and subjected to vertical one-pass butt welding in using electro-gas welding (EGW) or electro-slag welding (ESW) having welding heat inputs of 20 to 100 kJ/mm. Then, in the HAZ located at the center portion of the plate thickness ( $t/2$ ), notches were formed at two locations, that is, the HAZ separated from the FL (Fusion Line) by 1 mm (HAZ 1 mm) and the FL. A Charpy impact test was conducted at  $-40^{\circ}\text{C}$ . Table 2 shows the welding conditions and HAZ toughnesses. In the Charpy impact test here, use was made of JIS No. 4 2 mm V-notch full size test pieces. Further, Table 2 also describes the former austenite grain size in FL-HAZ 1 mm. The "former austenite grain size in FL-HAZ 1 mm" described here is the average grain size obtained by measuring the grain size of the former austenite grains contained within a 2 mm range in the thickness direction centered by  $t/2$  and the FL-HAZ 1 mm range by the cross-sectional method. Note that, the measurement was conducted by using particulate ferrite connected in a form of a net as the grain boundaries of the former austenite grains.

D1 to D49 are steels of the present invention. The chemical compositions of the steels are properly controlled, therefore the large heat input HAZ toughness at  $-40^{\circ}\text{C}$  is good while satisfying the predetermined base material performances. Further, in D23-D31 and D46-D49 obtained by dispersing the fine oxide particles, the former austenite grain size in FL-HAZ 1 mm becomes finer than those of the others, i.e.  $200\text{ }\mu\text{m}$  or less, and the large heat input HAZ toughness at  $-40^{\circ}\text{C}$  becomes further higher. Further, D20 aiming at increasing the refined HAZ



structure by adding B has a better HAZ toughness in comparison with D19 without addition of B and containing addition elements other than B in the equal amounts and exhibits a higher performance for also the large heat input HAZ toughness at -40°C.

On the other hand, the Comparative Steels C1 to C17 do not contain sufficient Ni for satisfying equation [1] or properly control the chemical compositions of the steels, so the large heat input HAZ toughness is insufficient.

Table 1

Class	Sym.	C	Si	Mn	P	S	Ni	Nb	Al	Ti	N	Ca	Mg
Inv. steel	D1	0.04	0.13	1.31	0.008	0.002	1.6	0.006	0.015	0.008	0.0035		
	D2	0.04	0.17	0.81	0.008	0.002	2.8	0.006	0.015	0.008	0.0035		
	D3	0.07	0.17	1.40	0.007	0.002	0.9	0.006	0.015	0.007	0.0035		
	D4	0.07	0.05	0.81	0.006	0.002	2.4	0.006	0.014	0.008	0.0035		
	D5	0.10	0.19	1.11	0.007	0.002	1.1	0.004	0.015	0.007	0.0032		
	D6	0.13	0.05	0.91	0.007	0.003	1.2	0.005	0.014	0.006	0.0037		
	D7	0.06	0.19	1.14	0.007	0.002	1.3	0.005	0.012	0.006	0.0042		
	D8	0.06	0.22	1.11	0.006	0.003	2.1	0.005	0.014	0.006	0.0035		
	D9	0.09	0.15	1.21	0.007	0.003	1.4	0.006	0.015	0.006	0.0035		
	D10	0.12	0.11	1.01	0.007	0.002	1.4	0.005	0.014	0.009	0.0035		
	D11	0.13	0.14	0.91	0.006	0.002	1.5	0.006	0.015	0.008	0.0035		
	D12	0.06	0.14	1.41	0.007	0.002	1.6	0.005	0.014	0.008	0.0032		
	D13	0.06	0.22	1.11	0.007	0.002	2.4	0.005	0.014	0.007	0.0035		
	D14	0.09	0.21	1.31	0.008	0.002	1.4	0.005	0.014	0.008	0.0035		
	D15	0.13	0.19	1.01	0.007	0.002	1.6	0.005	0.014	0.007	0.0035		
	D16	0.12	0.22	0.91	0.007	0.003	2.1	0.006	0.015	0.006	0.0035		
	D17	0.13	0.17	1.01	0.006	0.002	1.7	0.005	0.014	0.006	0.0032		
	D18	0.12	0.15	1.11	0.008	0.002	1.5	0.005	0.014	0.006	0.0037		
	D19	0.06	0.14	1.41	0.007	0.002	1.6	0.005	0.014	0.009	0.0041		
	D20	0.06	0.14	1.40	0.007	0.002	1.6	0.005	0.014	0.009	0.0041		
	D21	0.06	0.10	1.21	0.007	0.002	1.7	0.006	0.015	0.010	0.0035		
	D22	0.06	0.22	1.11	0.007	0.002	1.8	0.005	0.014	0.008	0.0055		
	D23	0.06	0.16	1.31	0.008	0.004	1.8	0.005	0.014	0.008	0.0035	0.0018	
	D24	0.06	0.17	1.40	0.008	0.004	1.6	0.005	0.014	0.008	0.0037	0.0019	
	D25	0.06	0.12	1.20	0.007	0.002	2.1	0.006	0.015	0.007	0.0033		0.0016
	D26	0.06	0.15	1.00	0.007	0.002	2.6	0.005	0.014	0.008	0.0036		
	D27	0.06	0.11	1.21	0.007	0.002	1.8	0.015	0.015	0.007	0.0035	0.0014	
	D28	0.06	0.23	1.00	0.007	0.002	1.9	0.005	0.014	0.006	0.0035	0.0018	
	D29	0.06	0.17	1.20	0.008	0.004	1.8	0.005	0.014	0.006	0.0035	0.0036	
	D30	0.06	0.12	1.20	0.007	0.002	1.7	0.006	0.015	0.006	0.0035	0.0009	
	D31	0.06	0.12	1.20	0.007	0.002	1.9	0.006	0.015	0.006	0.0035	0.0016	
	D32	0.07	0.15	1.21	0.007	0.003	1.4	0.028	0.014	0.009	0.0032	0.0015	
	D33	0.08	0.13	1.21	0.009	0.002	1.3	0.013	0.014	0.010	0.0052	0.0017	
	D34	0.08	0.19	1.21	0.008	0.003	1.5	0.013	0.025	0.008	0.0076	0.0012	
	D35	0.08	0.19	1.21	0.010	0.002	1.2	0.021	0.014	0.008	0.0035		

Table 1 continuation 1

Class	REM	O	B	Cu	Cr	Mo	V	Ceq	Nl/Mn	10xCeq-3	Judg.*
Inv. steel								0.37	1.22	0.7	O
								0.36	3.46	0.6	O
								0.36	0.64	0.6	O
								0.37	2.96	0.7	O
								0.36	0.99	0.6	O
								0.36	1.32	0.6	O
								0.38	0.92	0.8	O
								0.39	1.89	0.9	O
								0.39	1.16	0.9	O
								0.38	1.39	0.8	O
								0.38	1.65	0.8	O
								0.40	1.13	1.0	O
								0.41	2.16	1.1	O
								0.40	1.07	1.0	O
								0.41	1.58	1.1	O
								0.41	2.31	1.1	O
								0.41	1.68	1.1	O
								0.41	1.35	1.1	O
								0.40	1.13	1.0	O
			0.0012					0.40	1.14	1.0	O
				0.4				0.40	1.40	1.0	O
			0.0023		0.2			0.41	1.62	1.1	O
		0.0019						0.40	1.37	1.0	O
		0.0019	0.0008					0.40	1.14	1.0	O
		0.0017	0.0009					0.40	1.75	1.0	O
	0.0220	0.0020	0.0011					0.40	2.60	1.0	O
		0.0017		0.3				0.40	1.49	1.0	O
		0.0030	0.0009		0.2		0.017	0.40	1.90	1.0	O
		0.0029	0.0009	0.3				0.40	1.50	1.0	O
		0.0028	0.0009	0.2		0.05		0.40	1.42	1.0	O
		0.0023	0.0009	0.2			0.037	0.41	1.58	1.1	O
		0.0018	0.0012	0.4				0.39	1.16	0.9	O
		0.0020	0.0009	0.3				0.39	1.07	0.9	O
		0.0015	0.0035	0.4				0.41	1.24	1.1	O
								0.36	0.99	0.6	O

Table 1 continuation 2

Class	Sym.	C	Si	Mn	P	S	Ni	Nb	Al	Ti	N	Ca	Mg
Inv. steel	D36	0.09	0.19	1.21	0.010	0.003	1.5	0.015	0.015	0.008	0.0035		
	D37	0.10	0.19	1.11	0.006	0.002	1.9	0.015	0.035	0.007	0.0035		
	D38	0.11	0.14	0.91	0.006	0.003	1.7	0.031	0.014	0.008	0.0035		
	D39	0.12	0.14	1.11	0.008	0.002	1.8	0.029	0.032	0.007	0.0032		
	D40	0.10	0.14	1.21	0.009	0.002	1.6	0.030	0.014	0.006	0.0037		
	D41	0.10	0.24	1.21	0.006	0.002	1.5	0.031	0.028	0.006	0.0042		
	D42	0.08	0.24	1.31	0.005	0.003	1.6	0.032	0.014	0.006	0.0035		
	D43	0.03	0.22	1.31	0.008	0.003	2.5	0.035	0.038	0.006	0.0035		
	D44	0.06	0.24	0.81	0.007	0.003	3.2	0.035	0.014	0.009	0.0035		
	D45	0.03	0.11	1.51	0.007	0.002	1.8	0.035	0.014	0.010	0.0035		
	D46	0.07	0.11	1.21	0.007	0.003	1.4	0.028	0.014	0.009	0.0032	0.0015	
	D47	0.07	0.28	1.21	0.007	0.003	1.4	0.028	0.014	0.009	0.0032	0.0015	
	D48	0.06	0.11	1.20	0.008	0.004	1.8	0.005	0.014	0.006	0.0035	0.0018	
	D49	0.06	0.28	1.20	0.008	0.004	1.8	0.005	0.014	0.006	0.0035	0.0017	
Comp. Steel	C1	0.04	0.14	1.90	0.007	0.002	0.1	0.008	0.012	0.008	0.0032		
	C2	0.04	0.09	1.60	0.006	0.003	0.8	0.009	0.019	0.008	0.0037		
	C3	0.06	0.09	1.70	0.007	0.003	0.2	0.005	0.012	0.008	0.0042		
	C4	0.09	0.11	1.60	0.008	0.003	0.0	0.006	0.015	0.007	0.0035		
	C5	0.10	0.14	1.30	0.008	0.002	0.7	0.005	0.014	0.008	0.0035		
	C6	0.13	0.22	1.20	0.007	0.002	0.5	0.003	0.012	0.008	0.0035		
	C7	0.06	0.11	1.90	0.007	0.002	0.1	0.006	0.015	0.008	0.0035		
	C8	0.06	0.14	1.60	0.007	0.004	0.8	0.005	0.014	0.007	0.0032		
	C9	0.09	0.17	1.40	0.008	0.002	0.9	0.005	0.014	0.008	0.0037		
	C10	0.11	0.23	1.30	0.007	0.002	0.8	0.006	0.015	0.007	0.0042		
	C11	0.06	0.16	2.00	0.008	0.004	0.1	0.005	0.014	0.006	0.0035		
	C12	0.06	0.11	1.60	0.007	0.002	1.1	0.006	0.015	0.006	0.0035		
	C13	0.10	0.25	1.70	0.006	0.003	0.2	0.006	0.015	0.006	0.0035		
	C14	0.12	0.14	1.40	0.007	0.002	0.7	0.005	0.014	0.006	0.0035		
	C15	0.09	0.12	1.60	0.008	0.003	0.8	0.015	0.013	0.009	0.0032		
	C16	0.08	0.24	1.50	0.008	0.003	0.6	0.035	0.013	0.010	0.0037		
	C17	0.09	0.14	1.20	0.007	0.002	1.4	0.045	0.014	0.008	0.0042		

Table 1 continuation 3

Class	REM	O	B	Cu	Cr	Mo	V	Ceq	Ni/Mn	10xCeq-3	Judg.*
Inv. steel						0.03		0.40	1.24	1.0	O
								0.41	1.71	1.1	O
							0.045	0.38	1.87	0.8	O
								0.43	1.62	1.3	O
				0.2				0.42	1.32	1.2	O
								0.40	1.24	1.0	O
								0.41	1.22	1.1	O
								0.42	1.91	1.2	O
								0.41	3.95	1.1	O
								0.40	1.19	1.0	O
		0.0018		0.4				0.39	1.16	0.9	O
		0.0018		0.4				0.39	1.16	0.9	O
		0.0026	0.0012	0.3				0.40	1.50	1.0	O
		0.0026	0.0012	0.3				0.40	1.50	1.0	O
Comp. steel								0.36	0.05	0.6	X
								0.36	0.50	0.6	X
								0.36	0.12	0.6	X
								0.36	0.00	0.6	X
								0.36	0.54	0.6	X
								0.36	0.42	0.6	X
								0.38	0.05	0.8	X
								0.38	0.50	0.8	X
								0.38	0.64	0.8	X
								0.38	0.62	0.8	X
								0.40	0.05	1.0	X
								0.40	0.69	1.0	X
								0.40	0.12	1.0	X
								0.40	0.50	1.0	X
								0.41	0.50	1.1	X
								0.37	0.40	0.7	X
								0.38	1.17	0.8	O

\*O is described where  $Ni/Mn \geq 10 \times Ceq-3$  is satisfied, and X is described where it is not satisfied.

Table 2

Class	Symbol	Production method	Plate thickness (mm)	Base material (t/2) <sup>1)</sup>			Number <sup>2)</sup> of oxide particles (per mm <sup>2</sup> )
				Tensile strength (Mpa)	Yield stress (Mpa)	VE <sub>40(J)</sub>	
Inv. steel	D1	TMCP	60	576	476	231	
	D2	TMCP	65	565	465	229	
	D3	DQ-T	70	576	456	225	
	D4	TMCP	60	576	476	231	
	D5	DQ-T	55	605	485	238	
	D6	TMCP	65	565	465	229	
	D7	TMCP	70	560	460	219	
	D8	TMCP	80	541	441	213	
	D9	DQ-T	60	601	481	225	
	D10	TMCP	65	570	470	223	
	D11	TMCP	75	550	450	216	
	D12	TMCP	80	545	445	208	
	D13	TMCP	55	596	496	224	
	D14	DQ-T	65	595	475	217	
	D15	TMCP	70	566	466	213	
	D16	TMCP	65	578	478	214	
	D17	DQ-T	70	588	468	211	
	D18	TMCP	75	556	456	210	
	D19	TMCP	70	565	465	214	
	D20	TMCP	70	575	482	214	
	D21	DQ-T	70	585	465	214	
	D22	TMCP	70	566	466	213	
	D23	TMCP	65	575	475	218	900
	D24	DQ-T	60	605	485	221	1200
	D25	TMCP	70	565	465	214	1300
	D26	TMCP	80	545	445	209	1100
	D27	TMCP	70	565	465	214	900
	D28	TMCP	65	574	474	218	1800
	D29	TMCP	60	585	485	221	2100
	D30	DQ-T	65	594	474	218	2400
	D31	TMCP	60	587	487	219	1900
	D32	TMCP	70	563	463	217	700
	D33	TMCP	65	572	472	221	600
	D34	DQ-T	80	567	447	207	1400
	D35	TMCP	70	555	455	225	

Table 2 continuation 1

Class	one-pass butt welding condition <sup>3)</sup>		Average $\gamma$ grain size in FL-HAZ 1 mm ( $\mu\text{m}$ ) <sup>4)</sup>	HAZ toughness <sup>5)</sup>	
	Welding method	Heat input (kJ/mm)		FL/vE <sub>-40</sub> (J)	FL+1mm/vE <sub>-40</sub> (J)
Inv. steel	EGW	39	480	140	128
	EGW	42	520	135	124
	ESW	85	770	116	106
	ESW	73	660	123	113
	ESW	67	605	127	117
	EGW	42	520	135	124
	ESW	85	770	116	106
	EGW	51	640	124	114
	EGW	39	480	140	128
	ESW	79	715	119	109
	EGW	48	600	128	117
	EGW	51	640	124	114
	EGW	35	440	144	132
	ESW	79	715	119	109
	ESW	85	770	116	106
	EGW	42	520	135	124
	EGW	45	560	131	120
	EGW	48	600	128	117
	EGW	45	560	131	120
	EGW	45	560	171	156
	ESW	85	770	116	106
	EGW	45	560	184	180
	ESW	79	180	207	189
	EGW	39	165	214	196
	EGW	45	152	221	203
	EGW	51	185	204	187
	ESW	45	180	207	189
	ESW	79	167	213	195
	EGW	39	184	205	188
	EGW	42	165	214	196
	EGW	39	184	205	188
	EGW	45	180	207	189
	EGW	42	164	214	197
	ESW	98	180	196	180
	ESW	85	660	123	113

Table 2 continuation 2

Class	Symbol	Production method	Plate thickness (mm)	Base material (t/2 part) <sup>1)</sup>			Number <sup>2)</sup> of oxide particles (per mm <sup>2</sup> )
				Tensile strength (Mpa)	Yield stress (Mpa)	VE <sub>40(J)</sub>	
Inv. steel	D36	DQ-T	70	584	464	215	
	D37	TMCP	65	578	478	214	
	D38	TMCP	60	581	481	226	
	D39	TMCP	70	571	471	208	
	D40	DQ-T	80	570	450	203	
	D41	TMCP	70	565	465	214	
	D42	TMCP	65	576	476	216	
	D43	TMCP	60	589	489	217	
	D44	TMCP	65	577	477	215	
	D45	DQ-T	60	605	485	221	
	D46	TMCP	70	553	465	217	900
	D47	TMCP	70	579	481	217	400
	D48	TMCP	60	578	485	221	2300
	D49	TMCP	60	592	485	221	1500
Comp. steel.	C1	TMCP	70	556	456	225	
	C2	DQ-T	60	595	475	233	
	C3	TMCP	75	544	444	224	
	C4	TMCP	60	574	474	234	
	C5	TMCP	60	576	476	232	
	C6	TMCP	55	586	486	236	
	C7	DQ-T	60	601	481	226	
	C8	TMCP	60	580	480	227	
	C9	TMCP	60	581	481	226	
	C10	TMCP	60	580	480	227	
	C11	DQ-T	70	585	465	214	
	C12	TMCP	60	585	485	221	
	C13	TMCP	70	564	464	215	
	C14	TMCP	65	575	475	218	
	C15	TMCP	55	598	498	222	
	C16	DQ-T	65	588	468	226	
	C17	TMCP	60	581	481	226	

Table 2 continuation 3

Class	one-pass butt welding condition <sup>3)</sup>		Average $\gamma$ grain size of FL-HAZ 1 mm ( $\mu\text{m}$ ) <sup>4)</sup>	HAZ toughness <sup>5)</sup>	
	Welding method	Heat input (kJ/mm)		FL/vE-40 (J)	FL+1mm/vE-40 (J)
Inv. steel	ESW	85	605	127	117
	EGW	42	520	135	124
	ESW	73	770	116	106
	EGW	45	640	124	114
	EGW	51	480	140	128
	ESW	85	715	119	109
	EGW	42	600	128	117
	EGW	39	640	124	114
	EGW	42	440	144	132
	ESW	73	715	119	109
	EGW	45	145	225	206
	EGW	45	195	200	183
	EGW	39	164	214	236
	EGW	39	185	204	225
Comp. steel	ESW	85	770	36	25
	EGW	39	480	57	40
	EGW	48	600	46	32
	EGW	39	480	57	40
	EGW	39	480	57	40
	ESW	67	605	45	32
	EGW	39	480	57	40
	EGW	39	480	57	40
	EGW	39	480	57	40
	EGW	39	480	57	40
	ESW	85	770	36	25
	EGW	39	480	57	40
	EGW	45	560	49	34
	EGW	42	520	53	37
	ESW	67	605	45	32
	EGW	42	502	53	37
	EGW	39	480	57	40

1) Plate thickness center position; YS and TS are average values of two test pieces; Charpy absorption energy at -40°C (vE-40) is an average value of three test pieces.

2) Extraction replica was prepared from any portion of steel plate, and observed under electron microscope by X10000 magnification in 100 fields or more (10000  $\mu\text{m}^2$  or more in observation area). However, particles of less than 0.1  $\mu\text{m}$  were obtained at properly raising magnification. Particles are counted including oxide by elemental analysis among particles of equivalent circle diameter of 0.005 to 0.5  $\mu\text{m}$  and convert to number per 1  $\text{mm}^2$ .

3) EGW: Electro-gas welding; ESW: Electro-slag welding; Welding heat input is an average value in total length of welding; Common welding material is used in welding



processes

4) Average grain size of former austenite grains contained within a 2 mm range in the thickness direction centered by  $t/2$  and the FL-HAZ 1 mm range was measured by the cross-sectional method. Measurement was conducted by using particulate ferrite connected in a form of a net as the grain boundaries of the former austenite grains.

5) FL notches are layed down so as to equally divide WM and HAZ. vE-40- at each notch location is an average value of three test pieces.

As described above, the present invention provides thick steel plate satisfying the excellent toughness demands regarding destruction for ships, offshore structures, medium/high rise buildings, etc.